NANOSTRUCTURED CARBIDE CERMET POWDERS BY
HIGH ENERGY BALL MILLING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Application Serial No. 60/152,497, filed September 2, 1999, and to U.S. Application Serial No. 08/936,868, filed September 24, 1997, both of which are fully incorporated herein by reference.

BACKGROUND OF THE INVENTION

1.   Field of the Invention

5   This invention relates to carbide powders. In particular, this invention relates to a method for synthesizing micron- and submicron-sized, high purity, high surface area, cermet carbide powders from oxides using a high energy milling step.

2.   Brief Description of the Related Art

Micron-, submicron-, and nanosized carbide powders are important materials for

10   engineering applications. As used herein, "micron-sized" powders refers to powder particles wherein the mean particle size is equal to or greater than about 1.0 microns. "Submicron-sized" powders refers to powder particles wherein the mean particle size is in the range from about 0.1 to about 1.0 microns. "Nanosized" powders refers to powder particles wherein the mean particle size is less than about 0.1 micron (about 100 nm). In certain instances, micron-

and submicron-sized particles comprise many nanosized crystalline grains rather than a single, large grain. In these cases, the particles are referred to as "micron- and/or submicron-sized particles with nanostructures" or "micron- and/or submicron-sized, nanostructured particles." Nanosized and micron- and/or submicron-sized, nanostructured particles have a

5   high fraction of atoms located at the grain boundaries of the particle. Such materials accordingly have different, and often advantageous properties compared to conventional particles having the same chemical compositions.

Currently, the primary process for the production of micron- and submicron-sized carbide powders is high-temperature, carbothermic reduction of the corresponding oxides by

10   carbon powders. For example, most industrial silicon carbide (SiC) powders are manufactured via the Acheson process through carbothermic reduction of silicon dioxide (SiO_2) by carbon powder at temperatures up to 2000 to 2300°C for 30 hours. A carbothermic method based on reduction of one or more metal oxides reacted with a binder material and a source of carbon is disclosed in U.S. Patent No. 4,784,839 to Bachelard et al. Similarly, as

15   described in UK Patent No. 811,906 (issued in 1959), industrial titanium carbide (TiC) powders are produced through reduction of titanium dioxide (TiO_2) by carbon at temperatures ranging from 1700 to 2100°C for 10 to 20 hours.

Advantages of using high-temperature carbothermic reduction for the production of carbides include low cost of the oxide raw materials, and ease in scale-up for tonnage-level

20   production. However, the final products have a wide range of particle sizes, and moreover are normally larger than one micron, due to high reaction temperatures and long reaction times. Milling after carbothermic reduction is required. Undesirable inhomogeneities are also frequently found in the stationary reaction mix. These inhomogeneities are due to

-2-

diffusion gradients established during the reduction reaction, and require extensive milling

and purification procedures in order to convert the as-synthesized products into high quality,

sinterable powders. The SiC powder produced by the Acheson process, for example, has a

large grain size and is contaminated with oxygen. Accordingly, there remains a need in the

5   art for methods whereby homogenous carbide powders may be produced having a controlled

and uniform size, without extensive milling and purification procedures.

Cermet materials area of particular industrial interest. Tungsten cobalt carbide (WC-

Co), for example, is a well known carbide cermet, having been widely used in aluminum,

titanium, steel, aerospace, automobile, electronics, oil and wood industries, and in military

10   applications as metal-cutting tools, wire drawing dies, cold and hot rolls, punches and dies

for blanking and extrusion, bearing, micro-twist drills for printed circuit boards and printer

heads, complex components for aero engine fuel systems, rock-drilling bits, oil well drills,

large valves for controlling sludge in the oil industry, slip gauges, compacting tools,

measuring devices, fan blade and mixer blade cladding, hardfacings for a variety of wear

15   components, tire studs, armor-piercing projectiles, and other applications.

Currently, nanostructured WC-Co cermet powder is commercially manufactured by

the above-described conventional industrial process, or by spray conversion processing.

Spray conversion processing consists of (i) preparation and mixing of aqueous solutions of

the precursor compound ($CoCl_2$ as cobalt source and H_2WO_4 and $(NH_3)WO_4$ as tungsten

20   source); (ii) spray drying the aqueous solution to form a chemically homogeneous precursor

powder; and (iii) thermochemical conversion of the precursor powder to the nanostructured

end-product powder. The thermochemical conversion is conducted in a fluidized bed reactor

-3-

at 700 to 900°C in a Co/CO$_2$ atmosphere. The WC-Co powder produced is in the form of hollow, porous spheres 10-40 microns in diameter, comprising internal nanosized grains less than about 50 nm in diameter. There accordingly remains a need in the art for economical method for the manufacture of high quality, high surface area cermet materials such as

5   tungsten cobalt carbide.

SUMMARY OF THE INVENTION

The above-described drawbacks and deficiencies of the prior art are alleviated by a method for the manufacture of high purity, high surface area, carbide cermet powders, comprising high energy ball milling a mixture of precursor powders, followed by annealing the milled powder mixture. The precursor powders are selected from materials suitable for

10   the formation of cermets, for example silicon, titanium, thorium, hafnium, vanadium, chromium, tungsten, tantalum, niobium, and zirconium-containing materials. The precursors further include a source of carbon. Tungsten cobalt carbide powders produced by this method are submicron-sized (0.2 to 0.4 microns) with internal nanograins (10 to 40 nanometers in diameter). The synthesized powders may also include other nanophases such

15   as TiC, VC, TaC, NbC, and the like. These nanostructured WC-Co powders produced in accordance with this method have furthermore been shown to produce components with much better wear resistance than those made of conventional WC-Co powders.

Preferably, carbon monoxide is removed from the reaction chamber during heating in order to drive the reaction to completion at low temperatures and/or short times. The high

20   energy milling step serves to mix the oxide and carbon on a nanosized scale and to increase

-4-

the reactivity of the reactants by increasing surface area, introducing structural defects and

internal strains, and transforming the crystalline materials to an amorphous state. The

method produces high purity, high surface area, micron- or submicron-sized carbide powders

having a narrow particle size distribution and internal nanostructure. The method is

5   conducted at low temperatures, for short processing times, and thus significantly lowers cost.

The above discussed and other features and advantages of the present invention will

be appreciated and understood by those skilled in the art from the following detailed

description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph showing the inverse relationship between milling time and

10   crystallite size.

FIGURE 2 is a graph showing the relationship between milling time and specific

surface area.

FIGURE 3 shows the XRD patterns of WO_3-CoO-C powder milled for varying times

and then annealed at 800°C for 2 hours under argon.

15   FIGURE 4 shows changes in the XRD patterns of WO_3 and graphite powder milled

for three hours at 800°C and 900°C.

FIGURE 5 shows changes in the XRD pattern of CoO and graphite powder mixtures

before milling, after milling, and after milling and carbothermic reduction at 800°C under

argon for 2 hours.

FIGURE 6 shows the changes in XRD patterns of WO_3 and graphite powder with and without CoO, each annealed at 800°C for 2 hours.

FIGURE 7 shows the XRD patterns of a WO_3-CoO-C powder mixture milled for 12 hours at ambient temperature and then annealed at 900°C under argon for 0.5 hours and then under CO for 1.5 hours, illustrating the formation of nanostructured WC-Co cermets.

FIGURE 8 shows the XRD patterns of tungsten cobalt carbide powders milled with and without a liquid.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the present method, metal carbide powders are manufactured by first, high energy milling of selected oxide powders with carbon powder at ambient temperature for about 2 to 48 hours; and second, annealing the milled powders to produce the corresponding carbides. Heating the milled powder mixture at a temperature between 500 and 1500 °C for about one to two hours produces submicron-sized, nanostructured powders, while heating at a higher temperatures (about 1500 to about 1800 °C) will lead to grain growth and produce micron-sized powders. During heating, subatmospheric pressure or a flowing argon atmosphere is preferably maintained, thereby removing carbon monoxide gas from the reaction chamber and driving the reaction to completion. The high purity carbide powders thus produced comprise homogenous particles with a narrow particle size distribution.
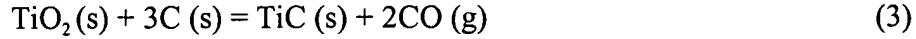
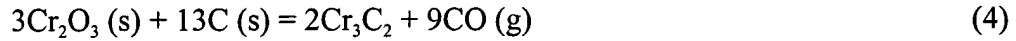The overall stoichiometric reaction for the method in accordance can be expressed generally as:

$$M_xO_y + (z + y)C = M_zC_z + yCO \qquad (1)$$

wherein M represents the metal element, and x, y and z are constants. Thus, for the synthesis of SiC, equation (1) becomes:

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \qquad (2)$$

5   Synthesis of TiC is:

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g) \qquad (3)$$

Synthesis of Cr_3C_2 is shown in equation (4):

$$3Cr_2O_3(s) + 13C(s) = 2Cr_3C_2 + 9CO(g) \qquad (4)$$

Carbides amenable to synthesis using the method of the present invention include, but

10   are not limited to, those based on silicon, titanium, thorium, hafnium, vanadium, chromium, tungsten, tantalum, niobium, zirconium, and the like, for example, SiC, TiC, VC, HfC, ThC_2, ThC, Cr_3C_2 WC, W_2C, ZrC, TaC, Ta_2C, and NbC. Carbide composite powders (of two or more carbides) may also be formed by high energy milling of the corresponding metal oxides and carbon. Adjustment of the molar ratio of the starting oxides leads to composite powders

15   having each of the carbides at a given volume fraction.

The first step requires high energy milling, i.e., ball milling, of selected oxide powders with a source of carbon for 2 to 48 hours at ambient temperature. The ball milling is preferably conducted in an inert atmosphere (e.g., an argon gas atmosphere) using methods and equipment known in the art, such as an attritor, vibratory mill, or horizontal ball mill.

20   Use of attritors and horizontal ball mills are preferable for tonnage-level production. The carbon source could be graphite, coal, , thermal black, acetylene black, coke, or combinations thereof, or other sources known in the art, depending on the required purity of the final products. The milling step is important in that it reduces all powder particles to submicron

-7-

size, transforms most of the powders to an amorphous state, and provides a uniform mixing

of carbon with oxides on a nanometer scale. Either wet or dry ball milling may be used. The

liquid used for wet milling is preferably inert under the milling conditions, for example a

hydrocarbon solvent such as heptane.

5   The key parameters for optimizing synthesis of high purity carbides during milling

include the ratio of the ball-to-powder weight (referred to herein as the charge ratio); the

milling time; the composition and purity of the starting materials; the cooling conditions

during milling; and the milling speed. The crystallite size of the as-milled powder mixture

decreases with increasing milling time and increase with increasing the molar ratio of

10   carbon:metal oxide. Reduction of the crystallite size of the as-milled powder in turn

enhances the formation kinetics of the carbides during the annealing step. Thus, where

annealing time and temperature are held constant, an increase in milling time results in finer

crystallite sizes and more uniform mixing, thereby resulting in an increase in the amount of

formed SiC.

15   The milled powders are next annealed, that is, heated at a specified temperature.

Heating in the range from between about 500°C to about 1500°C results in the formation of

submicron-sized, nanostructured carbides. Heating in the range from about 1500°C to about

1800°C results in the formation of micron-sized particles.

Annealing is preferably conducted under a flow of inert gas i.e., argon, or at reduced

20   pressure, preferably at less than 1000 millimeters. Either of these conditions will result in the

removal of carbon monoxide gas from the reaction chamber, thereby driving the reaction to

completion in about 1 to 2 hours. The reduced pressure should not be so low as to draw off

either the reactants or the product. An acceptable minimum pressure depends on the form of

-8-

reactants during the heating process, i.e., loose powder form or cold compacted (see Examples below).

The key parameters during annealing include the annealing temperature, the holding time, and the annealing atmospheric pressure. The formation of carbides is enhanced with

5   use of higher annealing temperatures and longer annealing times.

The above-described method has a number of advantages over prior art methods. For example, milling after the carbothermic reduction is eliminated. Powder handling, including loading and removal from the canister and the furnace, are carried out in air, which substantially decreases costs as compared to processes requiring powder handling under an

10   inert atmosphere.

The purity of the products is also increased. Although the XRD patterns of the annealed powders indicate the presence of both tungsten carbide and MC (M being a metal) in the final products, these contaminants derive from wear of the tungsten carbide balls and the wall of the canister used during high energy milling. Tungsten carbide contamination is

15   prevented by using balls made of the carbide identical to that being synthesized, for example, SiC balls used for production of SiC powders and TiC balls for production of TiC powders. Both of these balls are commercially available. The MC contamination is prevented by use of carbide canisters or carbide-lined canister. Furthermore, a short milling time could be employed to prevent the contamination, as in the following examples that only use 1.5-hour

20   milling times.

In another embodiment, high purity, high surface area carbide cermet powders may be provided by a method comprising high energy ball milling a mixture of precursor powders, followed by annealing the milled powder mixture. The precursor powders are selected from

-9-

materials suitable for the formation of cermets, for example silicon, titanium, thorium, hafnium, vanadium, chromium, tungsten, tantalum, niobium, and zirconium-containing materials. Exemplary carbides thus include WC, TiC, TaC, NbC and Cr_3C_2, and combinations of the foregoing carbides. Exemplary metals include cobalt and nickel-

5   chromium alloys, or a combination thereof.

Suitable precursor materials include but are not limited to the oxides and elemental forms of the materials for example tungsten, tungsten oxide, cobalt, cobalt oxide, titanium, titanium oxide, nickel, nickel oxide, and the like. The mixture of precursors further includes a source of carbon as described above.

10   Again, the carbide cermet powders are manufactured by high energy milling a mixture of precursors (e.g., WO_3 and CoO for making WC-Co cermets) with a carbon source for 2 to 24 hours, preferably at ambient temperature. The milling is conducted in an inert atmosphere (e.g., an argon gas atmosphere) or air using an attritor, vibratory mill, or horizontal ball mill. Attritors and horizontal ball mills are preferable for tonnage production.

15   Thigh energy milling reduces all powder particles to submicron (0.1 to less than 1.0 micron) or nanometer (10 to less than 100 nm) sizes, transforms some of the powders to an amorphous state, and provides a uniform mixing of carbon with oxides on nanometer scales. Either wet or dry ball milling may be used. The liquid used for wet milling is preferably inert under the milling conditions, for example a hydrocarbon solvent such as heptane. The key

20   parameters of the milling step for synthesizing high purity, nanostructured cermets are the charge ratio, the milling time, the composition of the starting powder mixture, the cooling condition during milling, and the milling speed.

The milled powder mixture is annealed at a temperature between about 500 to about 1500°C to form the cermet carbide powder. The key parameters during annealing are the atmosphere, the holding time, and the temperature. For tungsten cobalt carbide powders, for example, the annealing temperature is preferably between about 700 and about 1300°C for 1

5   to 2 hours to form nanostructured cermet WC-Co powders. The heating process is conducted in an atmosphere comprising argon (Ar), carbon monoxide (CO), hydrogen (H_2), or combinations thereof. Powder handling, including loading and removal from the canister and the furnace, is carried out in air; it does not require an inert atmosphere, which would substantially increase the cost of the process. The cermet powder so-produced is submicron-

10   sized (0.2 to 0.4 microns) with internal nanograins of 10 to 40 nm in diameter (see Examples 3 to 6).

It has been established that the crystallite size of the as-milled powder mixture decreases with increasing the charge ratio, the milling time (Figure 1), the molar ratio of the oxide to carbon, and the milling speed. The specific surface area (SSA) of the milled powder

15   increases with milling time at first, and then decreases after about 12 hours of milling; furthermore, the SSA of the milled powder is always higher than that of the starting powder mixture (Figure 2). Reducing the particle size, increasing the specific surface area, and achieving the uniform mixing between the oxide and carbon through high energy milling have enhanced carbothermic reduction to form tungsten and tungsten carbides. As shown in

20   Figure 3, conversion of WO^3 to W and then W to W_2C increases with increasing milling time.

The kinetics of WC formation are also strongly dependent on the temperature of carbothermic reduction, as shown in Figure 4.

In this embodiment, the metal binder in the cermet system can be added to the precursor powder mixture in the form of either the metal oxide (e.g., CoO) or elemental

5   metal (e.g., Co) powder. With respect to cobalt, the oxide is preferred because it is more brittle than the pure metal. Uniform mixing of WO_3, C, and CoO more readily achieved, which leads in turn to a uniform distribution of Co in the final product. CoO can be carbothermically reduced to elemental Co easily when the CoO and C mixture is heated to about 800°C, as shown if Figure 5. An important advantage of adding CoO (or Co) to the

10   powder mixture before milling is that Co is one of the best catalysts for the decomposition of carbon monoxide (CO). Decomposition of CO in turn provides active carbon for the reduction of the various oxides and carburizes elemental W and many intermediate compounds (e.g., W_2C, Co_6W_6C and Co_3W_3C) that may appear in this inventive process to form WC. The effect of Co is shown clearly in Figure 6 wherein WC formation with and

15   without Co is compared.

Similarly an elemental powder could also be used as the starting material in the formation of the carbide (e.g., tungsten could be used to instead of, or in combination with, tungsten oxide). With respect to tungsten, tungsten oxide is preferable because tungsten is more expensive than tungsten oxide, and because shorter milling times are required for

20   tungsten oxide.

The overall reactions for synthesizing WC-Co cermets can be expressed as

$$WO_3 + 4C = WC + 3CO \qquad\qquad (1)$$

$$CoO + C = Co + CO \qquad\qquad (2)$$

Tungsten cobalt carbide powders produced by this method are submicron-sized (0.2

to 0.4 microns) with internal nanograins (10 to 40 nanometers in diameter). The

5   nanostructured WC-Co powders produced in accordance with this method have furthermore

been shown to produce components with much better wear resistance than those made of

conventional WC-Co powders.

The synthesized powders may also include other phases such as TiC, VC, TaC, NbC,

and the like, to produce complex grade cermets such as WC-TiC-Co, WC-TaC-Co, WC-VC-

10   Co and WC-TiC-TaC-NbC-Co. Either the desired carbide(s) (e.g., TiC, TaC, VC, and NbC

powders) or their corresponding oxides (e.g., TiO_2, Ta_2O_5, V_2O_5, V_2O_3, Nb_2O_5, Nb_2O_3 and so

on) can be added to the WO_3, CoO, and C mixture before the high energy ball milling. The

temperature used in the annealing may also be adjusted, depending upon the nature of

additives. Nanostructured cermets with metallic binders other than Co can also be formed.

15   For example, to manufacture seal rings that are subjected to corrosive environments, the

binder can be changed to a nickel-chromium alloy. This can be accomplished by replacing

CoO with NiO and Cr_2O_3 and adjusting the amount of carbon accordingly.

In order to provide better understanding of the present invention, examples are set

forth below which are illustrative only. Those skilled in the art will recognize that there are

20   numerous modifications and variations, and that the present invention is not limited to such

examples.

EXAMPLES

Example 1: Synthesis of Nanocrystalline TiC

Anatase-TiO$_2$ powder (99.95% pure, mean diameter 0.3 μm, obtained from J. T.

Baker Chemical Co., Phillipsburg, NJ) is mixed with graphite powder (99.9% pure, mean

diameter less than 10 μm, obtained from Johnson Matthey, Ward Hill, MA) and tungsten

5   carbide balls (4.76 mm diameter) to prepare a powder and ball mixture having a molar ratio

of carbon:oxide of 4:1, and the charge ratio of the ball:powder weight of 60:1. This powder

and ball mixture is loaded into the milling canister of modified Szegvari attritor in

accordance with the procedure set forth in "Synthesis of Nanocrystalline SiC at Ambient

Temperature Through High Energy Reaction Milling", Z.-G. Yang and L. L. Shaw,

10   Nanostructured Materials, Vol. 7, pp. 873-886 (1996), incorporated herein by reference in its

entirety. Before milling, the charged canister is evacuated to 10^{-2} torr, flushed with argon,

evacuated, and then back-filled with argon having a of purity 99.95%, at a pressure of about

1.5 atm. The milling canister is then cooled using circulation water with a flow rate of about

770 mL/min, and this cooling is maintained throughout the process. The temperature of the

15   canister is monitored using an E-type thermocouple attached to the bottom of the canister.

The mixture is then milled using a milling speed of 600 RPM.

After milling for 24 hours, samples of the as-milled powder mixture are analyzed via

X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning election

microscopy (SEM), and surface area analysis. The XRD and TEM examination suggest that

20   the graphite powder has been transformed to an amorphous phase, and that while some of the

-14-

anatase-TiO$_2$ is amorphous, some also transforms to other polymorphic structures such as

rutile- and srilankite-TiO$_2$, and some retains anatase crystal structure, but is nanostructured

The as-milled powder is cold-compacted into a disc having a height of 2 mm and

diameter of 15 mm. The disc is heated to 1300°C at a heating rate of about 60°C/min, and

5   then held at the designated temperature under flowing argon gas having a of purity 99.95%

for 1 hour. The disc is then furnace-cooled to room temperature and removed from the

furnace.

X-ray diffraction analysis of the annealed specimen shows that nanocrystalline TiC

was formed from the milled powder mixture with no detectable TiO$_2$ or graphite. The

10   crystallite size, as determined from the line broadening of the XRD spectrum, is 26 nm, while

the particle size, as estimated from SEM, ranges from about 50-200 nm.

A comparative experiment shows that no TiC was formed if the TiO$_2$ and graphite

powders are simply mixed and then annealed in the absence of a high-energy milling

treatment. These data clearly indicate that the formation of TiC through the carbothermic

15   reduction of TiO$_2$ is greatly enhanced by high energy milling. Furthermore, the powder

particles are synthesized on submicron scale with nanostructures.

Example 2. Synthesis of Nanocrystalline SiC

SiO$_2$ (99.5% purity, mean diameter 2 μm, obtained from Johnson Matthey, Ward Hill,

MA) is mixed with graphite powder (99.9% purity, mean diameter less than 10 μm) and WC

20   balls (4.76 mm diameter) to prepare a powder and ball mixture having carbon:oxide molar

ratio of 4:1 and ball:powder charge of 60:1. This powder and ball mixture is milled using the

conditions described in Example 1 above. After milling for 1.5 hours, samples of the powder mixture are analyzed via XRD, TEM, SEM and surface area analysis. The XRD and TEM analysis indicate that some graphite powder is transformed to an amorphous phase, and that while some of the SiO_2 becomes amorphous, some remains crystalline.

5   The milled powder is loosely placed into an alumina boat and heated to 1500 °C at a heating rate of about 60 °C/min, and held at this temperature under an argon atmosphere for 1 hour. The annealed carbide is furnace cooled to room temperature and then removed from the furnace.

X-ray diffraction analysis of the annealed specimen shows that all silica has been

10   converted to nanocrystalline β-SiC. The crystallite size as determined from the line broadening of XRD spectrum is 19 nm, while the mean particle size as estimated from SEM is 290 nm. A comparative experiment under the same conditions but without the high energy milling step shows that no SiC is formed from the SiO_2 and graphite powder mixtures without the high energy milling.

15   Example 3. Synthesis of Nanostructured WC- 18% Co:

Tungsten trioxide (WO_3) powder of 99.8% purity (10 - 20 micrometer) was mixed with graphite (C) powder of 99.0% purity (~100 mesh) and cobalt oxide (CoO) powder of 95% purity (~300 mesh). The molar ratio of WO_3 : C : CoO was 1 : 5.24 : 0.677, which leads to a final product with a WC-Co composition comprising 18 wt.% Co. This powder mixture

20   was mixed with tungsten carbide (WC) balls to prepare a powder and ball mixture with a charge ration of 60:1. The powder and ball mixture was loaded into the milling canister of a

modified Szegvari attritor. The charged canister was evacuated up to 10^{-2} torr, flushed with

argon, followed by evacuation, and finally back filled with argon of purity 99.95% at a

pressure of 1.5 atm before the onset of milling. The canister was cooled with circulating

water at a flow rate of about 770 ml/min throughout the process and the temperature of the

5   canister was monitored using an E-type thermocouple attached to the bottom of the canister.

A milling speed of 600 RPM (the diameter of the canister = 88 mm) was employed.

After milling for 12 hours, the milled powder was taken out from the canister in air

and divided into two samples: one for XRD, SEM, TEM, and surface area analysis, and the

other for carbothermic reduction. For carbothermic reduction, the milled powder was loaded

10   loosely in a furnace, heated to 900°C with a heating rate of 500°C/hours, held in Ar for 0.5

hours, then in CO for 1.5 hours, and finally furnace cooled to room temperature and removed

from the furnace.

XRD analysis indicated that the crystallite size of WO_3 after milling for 12 hours was

20 nm. After carbothermic reduction, the milled powder was transformed to WC and Co

15   with no residual WO_3, CoO and C (Figure 7). Based on the peak broadening of XRD

patterns, the grain size of the synthesized WC was estimated to be 33 nm. The grain size of

Co was not estimated due to its low reflection intensity. The mean particle size of the WC-

Co cermet was 0.3 microns. Thus, the WC-18 wt.% Co cermet synthesized was submicron-

sized particles with internal nanograins.

20   Example 4. Synthesis of Nanostructured WC - 10 wt.% Co

The overall procedure and raw materials used in this example was the same as those in Example 3 except that the molar ratio of WO_3 : C : CoO was 1 : 5.24 : 0.347. The crystallite size of WO_3 after milling for 12 hours was found to be about 20 nm, similar to that found in Example 3. The grain size of the synthesized WC was estimated to be 28 nm,

5 slightly lower than that of the WC obtained in Example 3. Again, all WO_3, CoO and C were converted to WC and Co after the carbothermic reduction treatment.

Example 5. Synthesis of Nanostructured WC - 10 wt.% Co

The overall procedure and raw materials used in this example was the same as those in Example 4 except that carbothermic reduction was carried out at 1000°C. The grain size

10 of the synthesized WC was estimated to be 33 nm, slightly higher than the grain size of WC when carbothermic reduction was carried out at 900°C (Example 4).

Example 6. Synthesis of Nanostructured WC - 10 wt.% Co:

The overall procedure and raw materials used in this example was the same as those in Example 4, except that the powder mixture was only milled for 3 hours at ambient

15 temperature. The crystallite size of WO_3 after milling for 3 hours was found to be 23 nm, nearly identical to the size of WO_3 milled for 12 hours. All WO_3, CoO and C were converted to WC and Co after the carbothermic reduction treatment. The grain size of the synthesized WC was estimated to be 48 nm.

Example 7. Wet High Energy Ball Milling

Tungsten trioxide (WO_3) powder of purity 99.8% (10 – 20 micrometer) was mixed

with graphite (C) powder of purity 99.0% (-100 mesh) and cobalt oxide (CoO) powder of

purity 99% (-300 mesh). The molar ratio of WO_3 : C : CoO was 1 : 2.365 : 0.73, which

5   would lead to a final product with a compostion of WC – 18 wt.% Co. 150 ml of heptane

liquid was added to the foregoing powder mixture which was subsequently mixed with

tungsten carbide (WC) balls to prepare a powder and ball mixture and a charge ratio of 60:1.

The powder, ball and heptane mixture was loaded into the milling canister of a modified

Szegvari attritor the details of which can be found in our previous publication. The charged

10   canister was evacuated up to 10^{-2} torr, flushed with argon, followed by evactuation, and

finally back filled with argon of purity 99.95% at a pressure of 1.5 atm before the onset of

milling. The canister was cooled with circulating water at a flow rate of about 770 ml/min

throughout the process and the temperature of the canister was monitored using an E-type

thermocouple attached to the bottom of the canister. A milling speed of 600 RPM (the

15   diameter of the canister = 88 mm) was employed.

After milling for 6 hours, the milled powder was taken out from the canister in air and

was loaded loosely in a furnace, heated to 650°C with a heating rate of 500°C/h, held in an

atmosphere with 0.5 atm of H_2 and 0.5 atm of Ar for 2 hours, then at 800°C in a CO

atmosphere for 1 hour, and finally furnace cooled to room temperature and removed from the

20   furnace.

XRD analysis indicated that the crystallite size of WO_3 after milling for 6 hours was larger than that of WO_3 milled without the addition of heptane. Furthermore, substantial wear of WC balls was observed as shown by the curve (a) in Figure 8. After the carbothermic reduction at 800°C the crystallite size of WC was found to be about 8 nm.

5   Thus nanostructured WC/Co can be produced with the addition of heptane during high energy milling although contamination due to wear of balls increases and the efficiency of high energy milling decreases in comparison with high energy milling without the addition of heptane.

The present process is economical, and provides a replacement for the current

10   carbothermic reduction and spray conversion processes to manufacture carbide cermet powders. The process further allows the manufacture of nanostructured WC-Co cermets with lower costs and better performance. Therefore, the inventive process can have an immediate and significant impact on several industries that use WC-Co cermets.

While preferred embodiments have been shown and described, various modifications

15   and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

What is claimed is: